5-24-2016

Numerical simulation of hydrogen production by chemical looping reforming in a dual interconnected fluidized bed reactor

Piero Bareschino
Dipartimento di Ingegneria, Università degli Studi del Sannio, Italy, piero.bareschino@unisannio.it

Roberto Solimene
Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Italy

Giuseppe Diglio
Dipartimento di Ingegneria, Università degli Studi del Sannio, Italy

Erasmo Mancusi
Dipartimento di Ingegneria, Università degli Studi del Sannio, Italy

Francesco Pepe
Dipartimento di Ingegneria, Università degli Studi del Sannio, Italy

See next page for additional authors

Recommended Citation

Piero Bareschino, Roberto Solimene, Giuseppe Diglio, Erasmo Mancusi, Francesco Pepe, and Piero Salatino, "Numerical simulation of hydrogen production by chemical looping reforming in a dual interconnected fluidized bed reactor" in "Fluidization XV", Jamal Chaouki, Ecole Polytechnique de Montreal, Canada Franco Berruti, Wewstern University, Canada Xiaotao Bi, UBC, Canada Ray Cocco, PSRI Inc. USA Eds, ECI Symposium Series, (2016). http://dc.engconfintl.org/fluidization_xv/97

Authors
Piero Bareschino, Roberto Solimene, Giuseppe Diglio, Erasmo Mancusi, Francesco Pepe, and Piero Salatino

Università degli Studi del Sannio
Dipartimento di Ingegneria

Università degli Studi di Napoli Federico II
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale

Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche

Numerical Simulation of Hydrogen Production by Chemical Looping Reforming in a Dual Interconnected Fluidized Bed Reactor

Giuseppe Diglio, Piero Bareschino, Erasmo Mancusi, Francesco Pepe

Università degli Studi del Sannio, DING – Benevento (Italy)

Roberto Solimene

Consiglio Nazionale delle Ricerche, IRC – Napoli (Italy)

Piero Salatino

Università degli Studi di Napoli Federico II, DICMaPI- Napoli (Italy)

Introduction

H_2 as fuel can contribute to reduce CO_2 emissions

Currently H_2 is produced mainly by SMR

- Highly energy demand
- Need of post-processing for CO_2 separation

CLR can overcome these issues

- Which type of reactor configuration?
- Which type of oxygen carrier?

Numerical simulation

Aim of the work

Literature

Most of numerical simulations of CLR in DIFB are focused only on kinetic scheme

What you need?

An appropriate hydrodynamic model of the whole system in order to point out “stable” operating conditions.

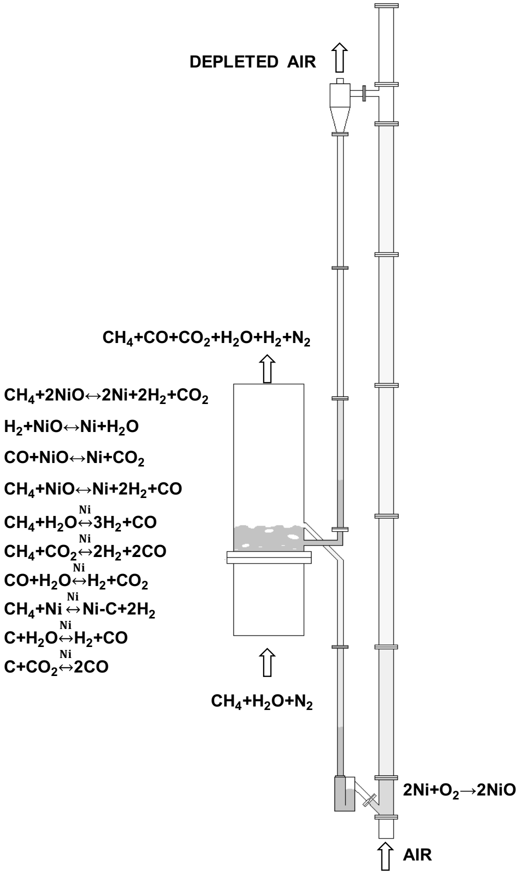
Aim of the work

To develop a simple mathematical tool coupling a CLR reactive scheme and a simple hydrodynamic model of a DIFB system.

Mathematical Model: hypothesis

1. FR split in two zones: dense zone below diluted zone/FreeBoard (FB)
2. Dense zone is modelled as a CSTR, while FB is modelled as a PFR
3. AR is modelled as CSTR (dense regime) or PFR (diluted regime)
4. Conversion is uniform throughout solid particles
5. In the FB only homogeneous WGS was taken into account

Mathematical Model: hydrodynamic model (I)



$CH_4+CO+CO_2+H_2O+H_2+N_2$

$CH_4+2NiO \leftrightarrow 2Ni+2H_2+CO_2$

$H_2+NiO \leftrightarrow Ni+H_2O$

$CO+NiO \leftrightarrow Ni+CO_2$

$CH_4+NiO \leftrightarrow Ni+2H_2+CO$

$CH_4+H_2O \overset{Ni}{\leftrightarrow} 3H_2+CO$

$CH_4+CO_2 \overset{Ni}{\leftrightarrow} 2H_2+2CO$

$CO+H_2O \overset{Ni}{\leftrightarrow} H_2+CO_2$

$CH_4+Ni \overset{Ni}{\leftrightarrow} Ni\text{-}C+2H_2$

$C+H_2O \overset{Ni}{\leftrightarrow} H_2+CO$

$C+CO_2 \overset{Ni}{\leftrightarrow} 2CO$

$CH_4+H_2O+N_2$

$2Ni+O_2 \rightarrow 2NiO$

$$m_{inv} = m_{BFB} + m_{LS} + m_R + m_{D/LV}$$

$$m_{BFB} = (A_{BFB}/g) \cdot \Delta P_{BFB}$$

$$m_{LS} = (1-\varepsilon_m) \cdot \rho_P \cdot A_{SP} \cdot (L_s - I_{sc}) + (1-\varepsilon_m) \cdot \rho_P \cdot A_{SC} \cdot I_{SC} + (1-\varepsilon_R) \cdot \rho_P \cdot A_{RC} \cdot h_{RC}$$

$$m_R = (A_R/g) \cdot \Delta P_R$$

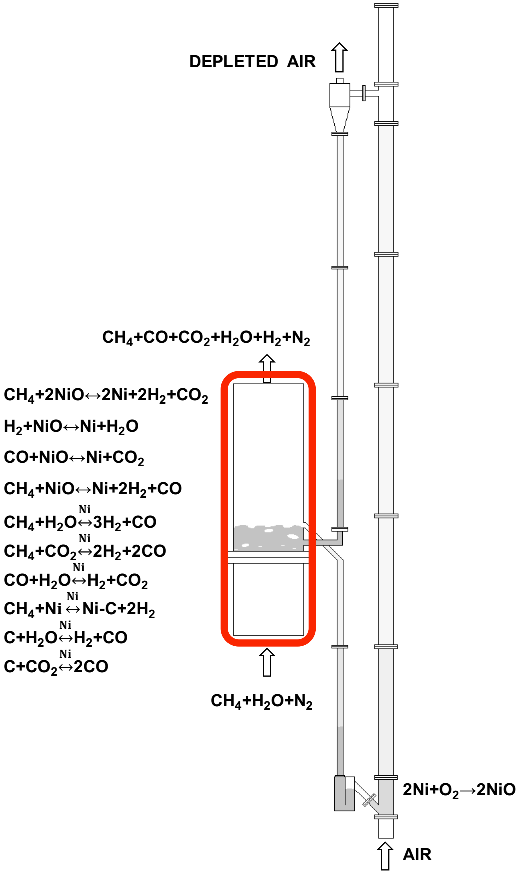
$$m_{D/LV} = (1-\varepsilon_H) \cdot \rho_P \cdot A_H \cdot L_H + (1-\varepsilon_V) \cdot \rho_P \cdot A_D \cdot [H \cdot \eta(L_V - H) + L_V \cdot \eta^*(H - L_V)]$$

$$\frac{dm_{D/LV}}{dt} = W_R - W_s$$

$$\frac{dm_R}{dt} = W_{LS} - W_R$$

$$\frac{dm_{LS}}{dt} = W_B - W_{Ls}$$

Mathematical Model: hydrodynamic model (II)



DEPLETED AIR

$CH_4+CO+CO_2+H_2O+H_2+N_2$

$CH_4+2NiO\leftrightarrow 2Ni+2H_2+CO_2$

$H_2+NiO\leftrightarrow Ni+H_2O$

$CO+NiO\leftrightarrow Ni+CO_2$

$CH_4+NiO\leftrightarrow Ni+2H_2+CO$

$CH_4+H_2O\overset{Ni}{\leftrightarrow}3H_2+CO$

$CH_4+CO_2\overset{Ni}{\leftrightarrow}2H_2+2CO$

$CO+H_2O\overset{Ni}{\leftrightarrow}H_2+CO_2$

$CH_4+Ni\overset{Ni}{\leftrightarrow}Ni\text{-}C+2H_2$

$C+H_2O\overset{Ni}{\leftrightarrow}H_2+CO$

$C+CO_2\overset{Ni}{\leftrightarrow}2CO$

$CH_4+H_2O+N_2$

$2Ni+O_2\rightarrow 2NiO$

AIR

Bubbling Fluidized Bed (BFB)

hp: elutriation is negligible

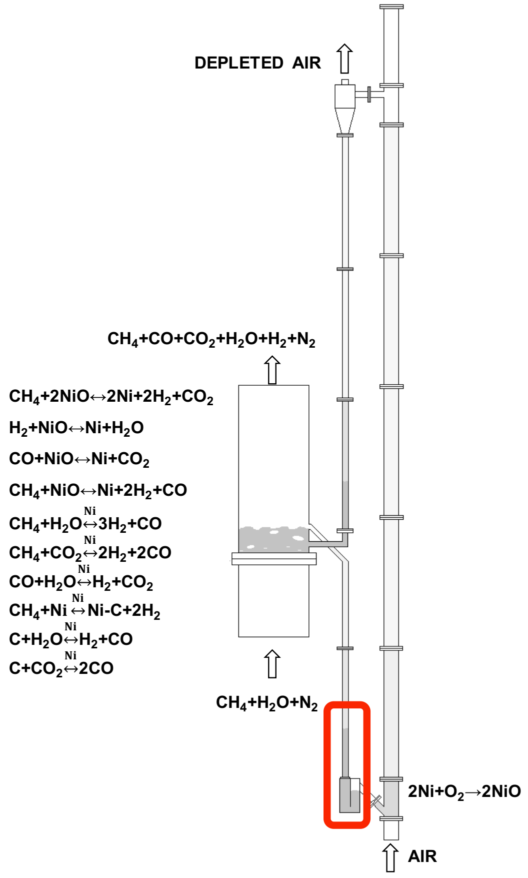
- Mass flow rate

$$W_B = \begin{cases} 0 & \rightarrow h_{D,B} < h_B \\ W_s & \rightarrow h_{D,B} \geq h_B \end{cases}$$

- Pressure drop

$$\Delta P_{BFB} = \rho_P \cdot (1-\varepsilon_D) \cdot g \cdot h_{D,B}$$

Mathematical Model: hydrodynamic model (III)



Loop Seal

Loop Seal works in complete fluidization condition between Supply Chamber (SC) and Recycle Chamber (RC).

- Mass flow rate

$$W_{LS}=W_s$$

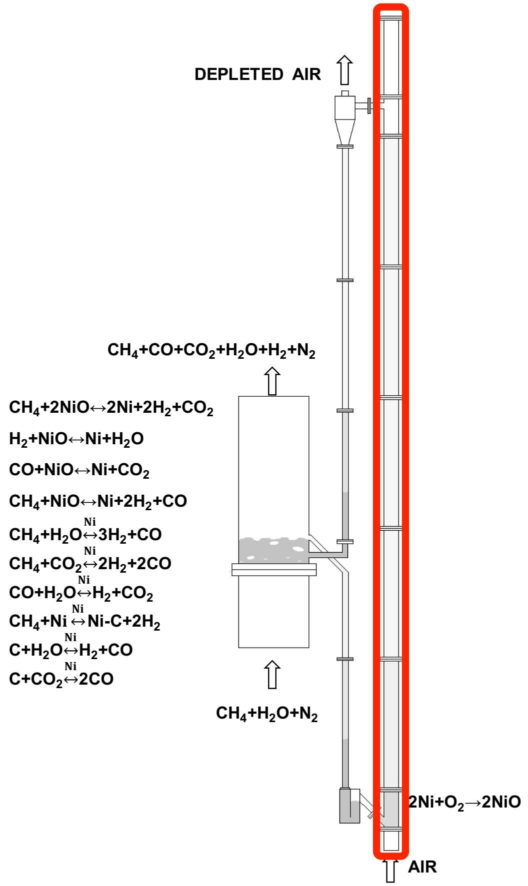
- Aeration gas flow rate

$$Q_{LS}=Q_{SC}+Q_{RC}$$

- Gas “leakage” between SC and RC

$$U_{Ls}\geq U_{mf}-\frac{W_R\cdot\varepsilon_{mf}}{A_{SC}\cdot\rho_P\cdot\left(1-\varepsilon_{mf}\right)}$$

Mathematical Model: hydrodynamic model (III)



DEPLETED AIR

$CH_4+CO+CO_2+H_2O+H_2+N_2$

$CH_4+2NiO \leftrightarrow 2Ni+2H_2+CO_2$

$H_2+NiO \leftrightarrow Ni+H_2O$

$CO+NiO \leftrightarrow Ni+CO_2$

$CH_4+NiO \leftrightarrow Ni+2H_2+CO$

$CH_4+H_2O \overset{Ni}{\leftrightarrow} 3H_2+CO$

$CH_4+CO_2 \overset{Ni}{\leftrightarrow} 2H_2+2CO$

$CO+H_2O \overset{Ni}{\leftrightarrow} H_2+CO_2$

$CH_4+Ni \overset{Ni}{\leftrightarrow} Ni\text{-}C+2H_2$

$C+H_2O \overset{Ni}{\leftrightarrow} H_2+CO$

$C+CO_2 \overset{Ni}{\leftrightarrow} 2CO$

$CH_4+H_2O+N_2$

$2Ni+O_2 \rightarrow 2NiO$

AIR

Riser

hp: 1) transition between dense and dilute phase takes place when mass flow rate approaches the value corresponding to its saturation carrying capacity; 2) the variation of voidage along the riser and with the mass flux have been neglected.

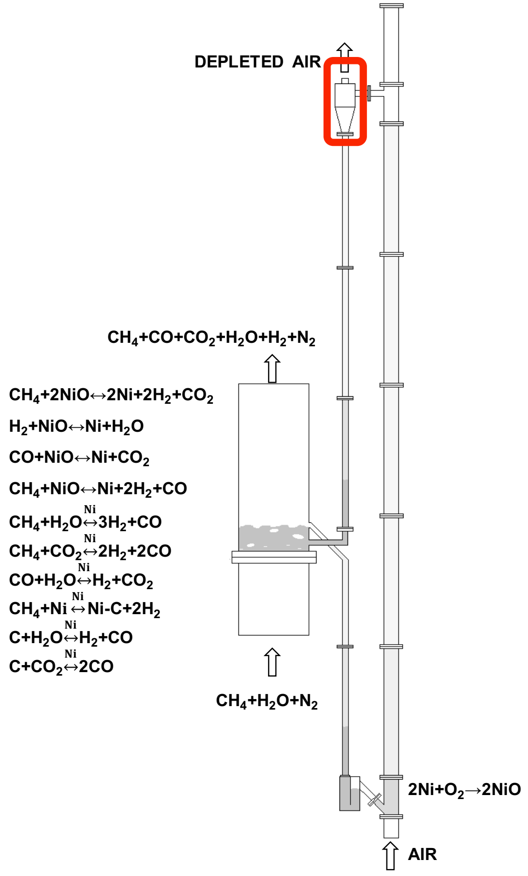
- Mass flow rate

$$G_s = \begin{cases} G_W = \beta \cdot \rho_P \cdot (1-\varepsilon_{mf}) \cdot U_R \rightarrow G_s \geq G_W \\ G_d = (U_S/h_R) \cdot (m_R/A_R) \qquad \rightarrow G_s < G_W \end{cases}$$

- Pressure drop

$$\Delta P_R = \rho_P \cdot (1-\varepsilon_D) \cdot g \cdot h_D + \frac{g \cdot W_R}{A_R \cdot U_S} \cdot (h_R - h_D)$$

Mathematical Model: hydrodynamic model (III)



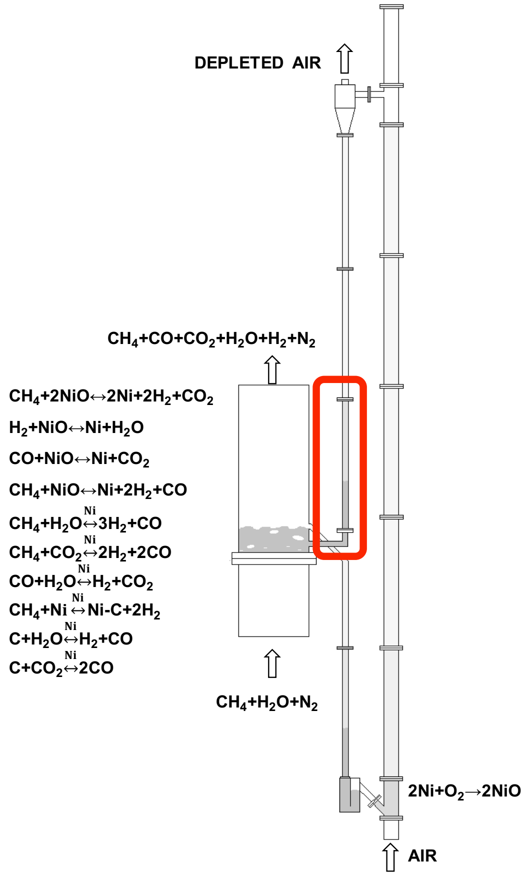
Cyclone

hp: Collection efficiency was assumed to be 1.

- Pressure drop

$$\Delta P_{CYC} = \rho_f \cdot K_C \cdot U_C$$

Mathematical Model: hydrodynamic model (III)



Downcomer/L-Valve

- Pressure drop

$$\frac{\Delta P_{DOW}}{H - L_E} = K_V \cdot (u_{fy} - u_{sy})$$

$$\frac{\Delta P_{LV}}{L_H} = K_H \cdot (u_{fx} - u_{sx})$$

$$\Delta P_{LV} = \frac{0.0649 \cdot {\rho_P}^{0.996} \cdot L_H}{{D_{LV}}^{0.574} \cdot {d_P}^{0.237}} \left(\frac{W_S}{A_R}\right)^{0.178}$$

- Aeration gas flow rate

$$Q_{LV} = Q_H + Q_V$$

Mathematical Model: kinetic scheme

OXIDATION REACTION	ΔH⁰, kJ/mol
R1) $2Ni + O_2 \rightarrow 2NiO$	-479

NON-CATALYTIC REDUCTION REACTIONS	ΔH⁰, kJ/mol
R2) $CH_4 + 2NiO \leftrightarrow 2Ni + 2H_2 + CO_2$	161
R3) $H_2 + NiO \leftrightarrow Ni + H_2O$	-2
R4) $CO + NiO \leftrightarrow Ni + CO_2$	-43
R5) $CH_4 + NiO \leftrightarrow Ni + 2H_2 + CO$	203

- Oxygen Carrier: **15 wt.% Ni/γ-Al_2O_3**
- Efficiency of air pre-heater: **90%**
- CH_4:H_2O is **3:1**
- FR is **isothermal**
- AR is **adiabatic**

CATALYTIC REDUCTION REACTIONS	ΔH⁰, kJ/mol
R6) $CH_4 + H_2O \overset{Ni}{\leftrightarrow} 3H_2 + CO$	206
R7) $CH_4 + CO_2 \overset{Ni}{\leftrightarrow} 2H_2 + 2CO$	247
R8) $CO + H_2O \overset{Ni}{\leftrightarrow} H_2 + CO_2$	-41
R9) $CH_4 + Ni \overset{Ni}{\leftrightarrow} Ni - C + 2H_2$	74
R10) $C + H_2O \overset{Ni}{\leftrightarrow} H_2 + CO$	131
R11))$C + CO_2 \overset{Ni}{\leftrightarrow} 2CO$	172

C. Dueso et al., Chem. Eng. J. 188 (2012) 142-154

I. Iliuta et al., AIChE J. 56 4 (2010) 1063–1079

F. Bustamante et al., AIChE J. 50 (2004) 1028–1041

F. Bustamante et al., AIChE J. 51 (2005) 1440–1454

Mathematical Model: mass and energy balances

Mass Balances

Dense regime/phase

$$Q_{k,in} \cdot C_{j,in} - Q_{k,out} \cdot C_{j,k} + m_{sc,k} \cdot \sum_i r_i \cdot \alpha_j = 0$$

$$W_{k,in} \cdot C_{sc,in} - W_{k,out} \cdot C_{sc,k} + M_{sc} \cdot m_{sc,k} \cdot \sum_i r_i \cdot \alpha_j = 0$$

Diluted regime/Free Board

$$\left(\frac{1}{A_k}\right)\frac{dn_{j,k}}{dh_k} = \sum_i r_i \cdot \alpha_j$$

Parameters

Operating conditions		**Properties of bed materials**	
$T_{fuel}\,[K]$	300	$\rho_p\,[kg \cdot m^{-3}]$	2540
$P[Pa]$	10^5	$d_p\,[m]$	$2.55 \cdot 10^{-4}$
$m_{inv}\,[kg]$	11.6	$\varepsilon_{mf}[-]$	0.445
$U_B\,[m \cdot s^{-1}]$	0.5	$\varepsilon_D[-]$	0.445
$U_R\,[m \cdot s^{-1}]$	2.7	$\varepsilon_B[-]$	0.445
$Q_{LV}\,[m^3 \cdot s^{-1}]$	$5.5 \cdot 10^{-5}$	$\varepsilon_V[-]$	0.423
$U_{LS}\,[m \cdot s^{-1}]$	$2U_{mf}$	$\varepsilon_H[-]$	0.488

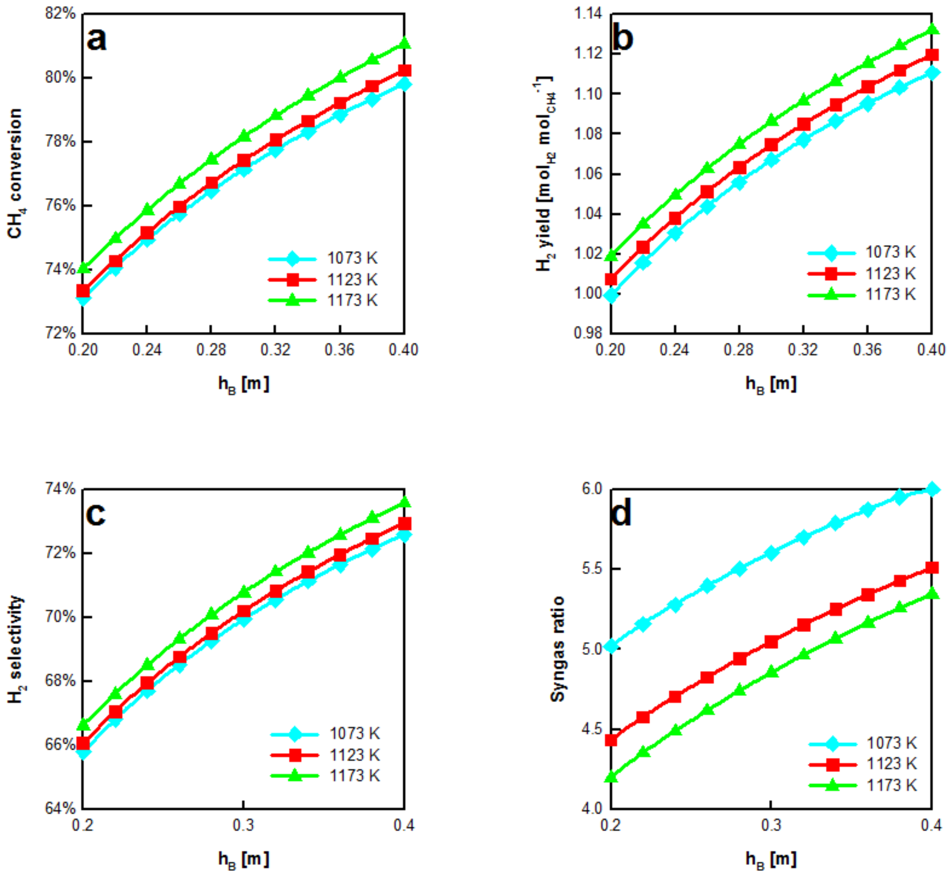
GEOMETRICAL CHARACTERISTICS

Riser		**L-valve**	
$D_R\,[m]$	0.102	$D_{LV}\,[m]$	0.04
$h_R\,[m]$	5.6	$L_H\,[m]$	0.4
BFB		$L_E\,[m]$	0.4
$D_B\,[m]$	0.12	**Cyclone**	
$h_B\,[m]$	2	$K_C\,[-]$	78
Downcomer		**Loop-Seal**	
$D_D\,[m]$	0.04	$A_{sc}\,[m^2]$	0.0025
$L_V\,[m]$	3.6	$h_{rc}\,[m]$	0.2

Energy balances

$$W_{k,in} \cdot \left[\sum_{sc}(1/M_{sc}) \cdot C_{sc,in} \cdot h_{sc,in}\right] - W_{k,out} \cdot \left[\sum_{sc}(1/M_{sc}) \cdot C_{sc,k} \cdot h_{sc,k}\right] + Q_{k,in} \cdot \left[\sum_j C_{j,in} \cdot h_{j,in}\right] - Q_{k,out} \cdot \left[\sum_j C_{j,k} \cdot h_{j,k}\right] + \sum_i \Delta H_{Ri} \cdot n_{j,k}^{Ri} = 0$$

Mathematical Model: results (I)



Fuel Reactor: effect of height of the BFB weir

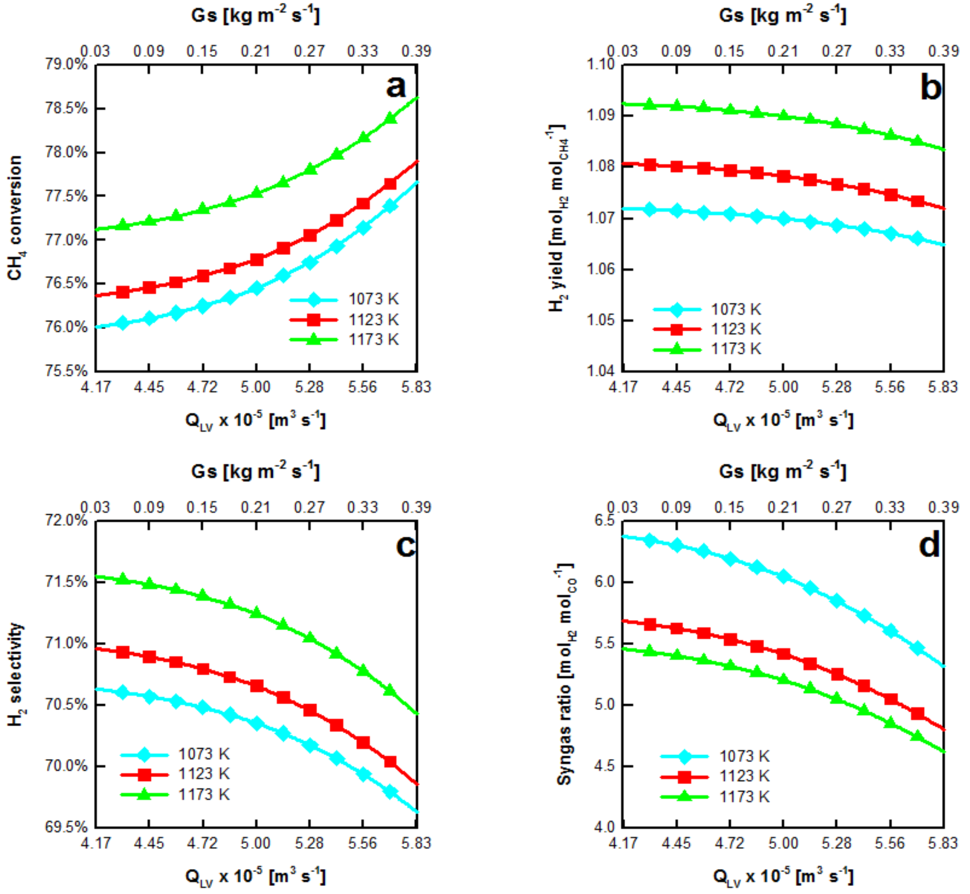
$$h_B \uparrow \gg m_{BFB} \uparrow \; and \; G_s \downarrow$$

so

$$\tau_{BFB} \uparrow \; and \; O_2 \downarrow$$

WGS reaction rate decreases with T

Mathematical Model: results (II)



Fuel Reactor: effect of solid circulation rate

$$G_s \uparrow \gg NiO: CH_4 \uparrow$$

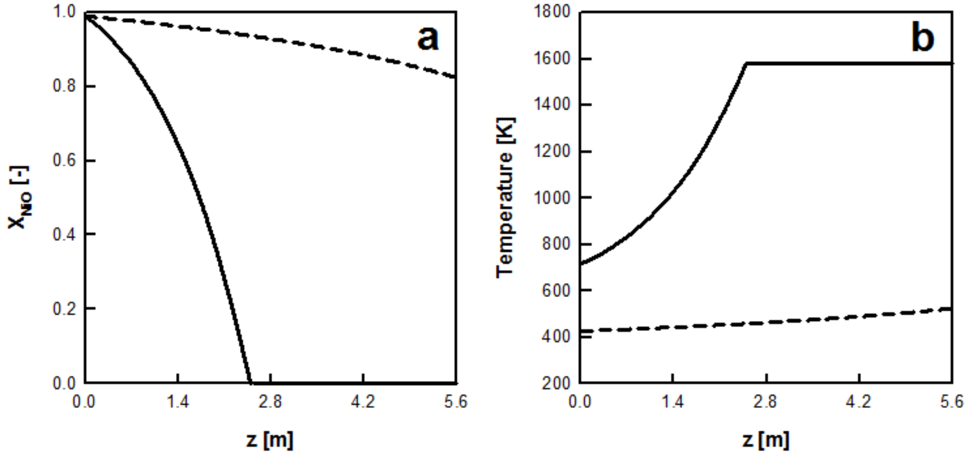
so

$$\eta_{CH_4} \uparrow and\ \eta_{H_2} \downarrow$$

$$\boxed{H_2 + NiO \leftrightarrow Ni + H_2O}$$

Mathematical Model: results (III)

Air Reactor: effect of inlet air pre-heat exchanger



Without pre-heat exchanger the temperature of inlet air is too low to drive Ni oxidation reaction

Conclusions

- A simple tool to evaluate the performance of a CLR process carried out in a DIFB was developed.
- The model is able to predict both main hydrodynamic variables and CLR performances.
- Higher H_2 production can be achieved reducing the amount of oxygen available in the FR decreasing solid circulation rate.
- If no air pre-heating is used, the temperature of air at the inlet of AR is too low to drive Ni oxidation reaction.